Naval Research Laboratory

Washington, DC 20375-5000

NRL Memorandum Report 6697

Purification of Metal Fluorides for the Ultra Low Loss Program

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August 6, 1990

REPORT DOCUMENTATION PAGE

Form Approved
OMB No 0704-0188

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	1990 August 6	

4. TITLE AND SUBTITLE

Purification of Metal Fluorides for the Ultra Low Loss Program

5. FUNDING NUMBERS

PE - 62234N
PR - 534047
TA - RS34047
WU - 65-2539-00

6. AUTHOR(S)

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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Naval Research Laboratory
4555 Overlook Avenue
Washington, DC 20375-5000

8. PERFORMING ORGANIZATION REPORT NUMBER

NRL Memorandum Report 6697

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Office of Naval Te[illegible]nology
Arlington, VA 22

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

By using radiotracer techniques the practical limits for the preparation of high purity ZrF_4, HfF_4, and LaF_3 via NRL current technology have been determined. The required concentration of impurities in BaF_2, AlF_3, and NaF for a 0.01 dB/km loss are calculated assuming the ZrF_4, HfF_4, and LaF_3 purification techniques are optimized to produce the impurity concentrations determined via radiotracer experiments.

The significance of this work to the Ultra-Low Loss Program is: 1. The radiotracer study has shown that current NRL technology is capable of producing ZrF_4, HfF_4, and LaF_3 which contain low to sub-ppb concentrations of transition and rare earth element impurities. 2. The calculated impurity concentrations for BaF_2, AlF_3, and NaF define a realistic goal for new purification techniques. 3. The required impurity levels in BaF_2, AlF_3, and NaF are achievable via current technology. Radiotracer results indicate sub-ppb concentrations of impurities are achievable in ZrF_4, HfF_4, and LaF_3, therefore, such levels should be possible in BaF_2, AlF_3, and NaF. This will be addressed in a future paper.

14. SUBJECT TERMS	15. NUMBER OF PAGES
	14
	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

NSN 7540-01-280-5500

Standard Form 298 (Rev-2-89)
Prescribed by ANSI Std 239-18
298-102

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PURIFICATION OF METAL FLUORIDES FOR THE ULTRA LOW LOSS PROGRAM

I. INTRODUCTION

In order to prepare a fluoride fiber exhibiting a loss of 0.01 dB/km the concentrations of the impurities Fe, Co, Ni, Cu, and Nd in the raw materials and the glass must be in the part-per trillion regime. A crucial question for the ultra low loss program's viability is whether materials of such high purity can be prepared and incorporated into a ZBLAN glass fiber? The purpose of this report is twofold; firstly determine where we are in purification technology with respect to our best purification techniques currently used for ZrF_4 and LaF_3 preparation, and secondly to determine the purity requirements for BaF_2, AlF_3, and NaF. Radioactive tracer techniques are used to predict the minimum impurity concentrations in zirconium and lanthanum fluorides prepared via recrystallization and coprecipitation, respectively. Assuming the minimum impurity concentrations in zirconium and lanthanum fluorides are achievable in actual practice the impurity levels in these materials can be fixed. Using this data the impurity concentrations in the other metal fluorides, BaF_2, AlF_3, and NaF are calculated.

The processes of recrystallization (ZrF_4, HfF_4), coprecipitation ($La(NO_3)_3$), and hydrofluorination (ZrF_4, HfF_4, LaF_3) have been studied experimentally by addition of radioactive tracers into key stages in the processing of these materials and following the distribution of the radioactive tracer as the purification process is carried out. In the present work, the radioactive tracers ^{59}Fe, ^{60}Co, ^{88}Y, and ^{139}Ce are added to the reaction media and the solution homogenized usually by stirring until the radioactive tracers are uniformly distributed throughout the solution. At this point it is assumed that the radioactive tracers cannot be chemically distinguished from their non-radioactive counterpart initially present in the raw material. Chemical processing is then carried out on the spiked solution and representative samples of the reaction products are taken. The distribution of the radioactive tracers between the two phases (in this case solid and liquid) is measured and expressed as a fraction of the total radioactive spike added, called the "spike fraction." The distribution of impurities after a single purification step on an unspiked sample is calculated by multiplication of the spike fraction by the known impurity concentration in an unspiked sample.

Using this data we can calculate the purification limits for the processes of recrystallization, coprecipitation and hydrofluorination. Once determined, these minimum impurity concentrations in ZrF_4 and LaF_3 can be used to calculate the impurity concentrations in BaF_2, AlF_3, and NaF required to achieve a loss of 0.01 dB/km. This step is significant in that for the first time we can use experimentally determined impurity concentrations on the sub-ppb order (via radiotracer) to fix the absorption contribution of two of the five components of ZBLAN glass.

Manuscript approved May 14, 1990.

II. EXPERIMENTAL

A. ZIRCONIUM/HAFNIUM FLUORIDE PURIFICATION TECHNIQUE.

1. Use high purity zirconium tetrachloride to prepare zirconium oxychloride.

$$ZrCl_{4(s)} + H_2O_{excess} \longrightarrow ZrOCl_{2(aq)}$$

The resulting zirconium oxychloride solution is then filtered through a 0.2 μm filter to remove particulates.

2. The filtered zirconium oxychloride solution is added to a 38% solution of HCl causing the zirconium oxychloride to recrystallize over a period of several hours.

3. The recrystallized zirconium oxychloride is then washed, pulped, and soaked with 7N HCl. The purified zirconium oxychloride is recovered by vacuum filtration. The recrystallization process is then repeated on the purified zirconium oxychloride.

4. Aqueous HF is then added directly to the recrystallized solid zirconium oxychloride. The solid dissolves rapidly and within 5 minutes a fine precipitate of zirconium fluoride monohydrate begins to form.

$$ZrOCl_{2(s)} + 4HF_{(aq)} \longrightarrow ZrF_4 \cdot H_2O_{(s)} + 2HCl_{(aq)}$$

The precipitate is allowed to age for 20 hours; it is then recovered via vacuum filtration. The purified zirconium or hafnium monohydrate is then dried in an oven at 110°c for 2 hours.

B. LANTHANUM FLUORIDE PURIFICATION TECHNIQUE

1. Use high purity lanthanum oxide with [Nd] = 7ppb. Purified via ion exchange at Ames Laboratory, Materials Preparation Center, Ames, Iowa.

2. Convert lanthanum oxide to lanthanum nitrate:

$$La_2O_{3(s)} + HNO_{3(excess)} \longrightarrow 2La(NO_3)_{3(aq)}$$

3. Add a small amount of concentrated ammonium hydroxide to the lanthanum nitrate solution prepared.

$$La(NO_3)_{3(aq)} + xNH_4OH_{(aq)} \longrightarrow (1-x/3)La(NO_3)_{3(aq)} + [(x/3)La(OH)_{3(s)} + \text{Impurities}]$$

D. The purified lanthanum nitrate is then converted to

lanthanum fluoride via addition of high purity hydrofluoric acid.

$$La(NO_3)_{3(aq)} + 3HF_{(aq)} \longrightarrow LaF_{3(s)} + 3HNO_{3(aq)}$$

III. Results and Discussion

1. Zirconium and Hafnium Fluoride Purification

The results of the radiotracer study for the recrystallization of zirconium oxychloride and its subsequent conversion into zirconium fluoride monohydrate are given in Table 1. The initial impurity concentrations in the zirconium oxychloride are from analysis of material purchased from Teledyne, Wah Chang. The impurity concentrations in the hydrofluoric acid were determined via Isotope Dilution - Inductively Coupled Plasma - Mass Spectrometry (ID-ICP-MS) at the National Institute of Standards and Technology (NIST)*. The overall results can be summarized as follows:

1. Two recrystallization steps of zirconium oxychloride reduce:
   a. Co, Ni, Cu, and Nd levels to sub ppb levels.
   b. Fe to below 5 ppb.
2. Hydrofluorination of the recrystallized zirconium oxychloride:
   a. Reduces all impurities to sub-ppb levels.
3. Loss contributed to the glass due to impurities, assuming $Fe^{3+}/Fe^{2+} = 50$, in zirconium fluoride is:

0.0016 dB/km

*Paulson, P.J.; Beary, E.S.; Bushee, D.S.; Moody, J.R. Anal. Chem. (1988) 60, 971-975. Analysis via Isotope Dilution Inductively Coupled Plasma - Mass Spectrometry.

2. Lanthanum Fluoride Purification

The results of the radiotracer study for purification via coprecipitation of lanthanum nitrate and its subsequent conversion into lanthanum fluoride are given in Table 2. The initial values for impurity concentrations in the lanthanum nitrate are of lanthanum oxide obtained from Ames Laboratory, Materials

Preparation Center, Iowa State University, Ames, Iowa. As in the case for zirconium fluoride purification NIST hydrofluoric acid impurity concentrations are used. The overall results can be summarized as follows:

1. Coprecipitation of a lanthanum nitrate solution:

   a. Reduces the concentration of Co and Ni to below 10 ppb.

   b. Reduces the concentration of Fe, Cu, and Nd to sub-ppb levels.

      o Initial [Nd] = 7 ppb via ion exchange at Ames Laboratory, Iowa State University.

2. Hydrofluorination of the $La(NO_3)_3$ solution incorporates the following amount of each impurity into the final fluoride:

   o 100% Fe, Ni, Cu, and Nd present in $La(NO_3)_3$ and HF solutions.

   o 60% Co present in $La(NO_3)_3$ and HF solutions.

3. Loss contributed to the glass, assuming Fe^{3+}/Fe^{2+} = 50, due to impurities in lanthanum fluoride is:

   0.0014 dB/km

3. Maximum Concentration of Impurities in Barium, Aluminum, and Sodium Fluorides

Using the radiotracer derived impurity concentrations for ZrF_4 and LaF_3 as real numbers the impurity concentrations in BaF_2, AlF_3, and NaF can be calculated for a fluoride fiber with 0.01 dB/km loss. The results of this calculation are given in Table 3 and the current analysis of NRL best materials are given in Table 4. The results in Table 3 were calculated using LOTUS software by varying the impurity concentrations in BaF_2, AlF_3, and NaF until the loss is approximately 0.01 dB/km. The results are not unique solutions and are interdependent, for example, if the neodymium concentration in BaF_2 is an order of magnitude lower than shown more neodymium could be tolerated in sodium fluoride. All materials in Table 4 were analyzed at NRL via Graphite Furnace Atomic Absorption Spectrometry (GFAAS) with the exception of aluminum fluoride which was analyzed via Spark Source Mass Spectrometry (SSMS). Results of the calculation can be summarized as follows:

1. The required impurity concentrations in these three materials are in the range; 0.3 - 1.0 ppb (ng/g).

   - o This gives a realistic target for evaluation of purification techniques.

2. Fe is at least an order of magnitude too high in BaF_2 and AlF_3

3. Cannot make any statement about the concentrations of impurities below instrumental detection limits.

   - o Currently working in improvement of detection limits.

IV. CONCLUSIONS:

This study has shown:

$\underline{ZrF_4/HfF_4}$

1. Using <u>available</u> HCl and HF zirconium fluoride can be prepared with <u>sub-ppb</u> levels of impurities. This translates into a loss in the fiber due to impurities carried by ZrF_4 of:

   <u>0.0016 dB/km</u>.

$\underline{LaF_3}$

1. Coprecipitation removes impurities in the order:

   Fe>>Cu>Nd>Ni>Co

2. Using <u>available</u> HF and $La(NO_3)_3$ purified via coprecipitation, LaF_3 can be prepared with Ni levels below 10 ppb and Fe, Co, Cu, and Nd at <u>sub-ppb</u> levels.

   - o Initial material must first be purified via ion exchange to remove Nd.

   - o $La(NO_3)_{3(aq)} + 3HF_{(aq)} \longrightarrow LaF_{3(s)}$ incorporation of oxide is a problem

3. The loss in the fiber due to impurities carried by LaF_3 is:

0.0014 dB/km.

Maximum Impurity Concentrations in BaF_2, AlF_3, and NaF.

1. Required purification range 0.3 - 1.0 ppb

   o BaF_2, AlF_3, and NaF

2. Fe very high in BaF_2 and AlF_3

3. Analytical development is required to lower detection limits for impurities.

TABLE I

ZIRCONIUM FLUORIDE PURIFICATION

RADIOTRACER STUDY

	CONCENTRATION, PPB				
COMPOUND	Fe	Co	Cu	Ni	Nd
$ZrOCl_2$	310	50	10	50	10
1 RECRYST.	16	3	0.5	3	0.5
2 RECRYST.	2	0.4	0.07	0.4	0.07
$HF_{(aq)}$	0.6	0.001	0.035	0.53	0.0003
$ZrF_4 \cdot H_2O$	0.27	0.05	0.012	0.09	0.068
LOSS (dB/Km)	5E-05	5E-04	2E-05	1E-04	9E-04

TOTAL LOSS (dB/Km) = 0.0016 dB/Km

$[Fe^{3+}/Fe^{2+} = 50]$

TABLE 2

LANTHANUM FLUORIDE PURIFICATION

RADIOTRACER STUDY

		Concentration, ppb				
		Fe	Co	Ni	Cu	Nd
$La(NO_3)_3$	Initial	1165	6	24	27	7
1 Coppt.		63	4	15	2	1.6
2 Coppt.		3.5	2.9	9.8	0.17	0.36
3 Coppt.		0.19	2	6.3	0.01	0.08
4 Coppt.		0.01	1.4	4	0.001	0.02

o Use Lanthanum Nitrate from Fourth Coprecipitation Step

	Fe	Co	Ni	Cu	Nd
$La(NO_3)_3$	0.01	1.4	4	0.001	0.02
$HF_{(aq)}$	0.6	0.001	0.53	0.035	0.0003
LaF_3	0.61	0.82	4.53	0.036	0.0203

Contribution, dB/km

Impurity	Loss Contribution, dB/km
Fe	1.0E-05
Co	7.7E-04
Ni	5.9E-04
Cu	5.9E-06
Nd	2.5E-05

Total loss contributed by LaF_3 in glass = 1.4E-03 dB/km

o Assuming $Fe^{3+}/Fe^{2+} = 50$

Table 3

Maximum Concentration of Impurities

In ZBLAN Components for 0.01 dB/km Loss

Concentration, ppb

	Fe	Co	Ni	Cu	Nd
ZrF_4[+]	0.27	0.05	0.09	0.012	0.068
BaF_2	1.0	0.5	0.5	0.5	0.3
LaF_3[+]	0.61	0.82	4.5	0.036	0.02
AlF_3	1.0	1.0	1.0	1.0	0.6
NaF	1.0	1.0	0.9	0.9	0.5

[+]Impurity concentrations achievable by current techniques as determined by radiotracer study.

TABLE 4

NRL BEST MATERIALS

Concentration, ppb

	Fe	Co	Ni	Cu	Nd
ZrF_4	<10	<10	<10	<10	<0.05
BaF_2	70	<21	<93	<9	unk.
LaF_3	<81	<32	<98	<73	7
AlF_3	60	<20	<30	<30	unk.
NaF	<49	<49	<74	<20	unk.

NOTE: The symbol < denotes that the impurity concentration is below the instrumental detection limit. All metal fluorides are analyzed by GFAAS except for AlF_3 which is analyzed by SSMS.

GFAAS - Graphite Furnace Atomic Absorption Spectrometry

SSMS - Spark Source Mass Spectrometry